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PROCEEDINGS

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# ADAPTATION OF WATER PRECONCENTRATION TECHNIQUES DEVELOPED FOR PCDD ANALYSIS TO OTHER TARGET ORGANIC POLLUTANTS.

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## Introduction

The analysis of water for organic pollutants involves preconcentration, isolation and detection steps which must be coordinated to produce acceptable detectivity and sensitivity in relevant concentration ranges. In this project, the development of a preconcentration apparatus, designed for isolation of dioxins, is being extended to a wider range of chlorinated hydrocarbons and pesticides in natural and treated waters. The modifications to the sampler are minor, requiring only the optimization of filtration cylinders and adsorption media. The isolation steps, however, require considerable development beyond the laborious and highly specialized procedures developed for the dioxins.

There are two major areas which require attention. First, the isolation procedures used for dioxins must be altered because they were designed to remove many of the eluted or extracted organic pollutants from detection which are now of interest. Secondly, the GC/MS detection procedures used for dioxins must now be broadened to observe the much larger number of compounds of interest.

The developments associated with adaptation of the automatic

preconcentration and traditional or supercritical isolation of compounds for detection are the subjects of the present research. The problems of broadening detection capabilities of GC/MS library identification routines require further attention and are beyond the scope of this paper.

## Experimental Design

Since the project is in its early stages, the experimental work is still in progress. Two directions of research are being undertaken.

### (1) Construction of Preconcentration Sampler

The sampler is an improved version of one developed for dioxin preconcentration which is currently under test by the Ministry of Environment. A schematic of water flow through the sampler is illustrated in figure 1. The overall design and placement of components is shown in figures 2 and 3.

The system is designed to provide two identical filtered and adsorbed samples of known volumes from a single source, without the introduction of external contamination. A water reservoir isolates the sampling unit from the water source by providing a physical break in the water flow. This sealed vessel only permits water flow in one direction through an electronically operated input valve. The internal air pressure is controlled through electronically operated valves, and extraneous air is exchanged through a charcoal filter.

The water is pumped past an optional injection port for controlled input of standard solutions, then into a helical mixing tube, and split into two sampling streams. These two streams pass through one or more removable filter chambers, as required, which contain tubular filters optimized for the particular water source. Each stream passes through a graphite gear pump and is brought to an operating pressure of about 20 psi. The streams then pass through visual flow meters and pressure gauges, and then to air release valves which permit the exclusion of air bubbles. This deaerated water is then pumped through removable XAD-2 resin adsorption columns. The two streams are recombined and pass through an electronic flow sensor which sends a signal to a digital flow meter to record the total flow rate. It is then exhausted through a final charcoal filter.

The filters and columns are prepared in the laboratory and can be installed in the sampler at the field site. Prior to each run, the total desired sample volume is established using a batch controller. The water system is first purged with source water, bypassing the filter and columns, and is then switched to sampling mode to be put under control of the batch computer. The flow rates are equalized manually by adjustment of the pump speed controls until the individual flow meters read identical values and the digital flow meter reads the desired total flow rate. The batch controller integrates the total volume and when the

preset value is achieved the system shuts off automatically. Automatic shutdown also occurs if pressure in the sampler exceeds 50 psi or falls below 3 psi, or if the housing to the filter or adsorption system is opened.

When sampling is completed, a recording of the flow rate throughout the run is obtained from a chart recorder. The filters and adsorption columns, which are isolated with self contained valves, are removed from the apparatus for transportation to the analytical laboratory.

The entire apparatus is housed in a self sealing case with the dimensions 1.5 m high x 0.5 m wide x 0.5 m deep, and weighing 75 kg. It is mounted on self contained wheels so it can be transported manually from site to site. Apart from the necessary connection to the water source and installation of filter chambers and adsorption columns, all functions are electronically controlled to eliminate dependence on manual operation.

(2) **Sample Isolation**

Samples received in filtration chambers and adsorption columns must be eluted and treated in the laboratory to isolate the compounds of interest. The two basic approaches to the processing of these samples are the traditional extraction with organic solvents and the more recent method of extraction using supercritical fluids.

The organic solvent method requires the use of a volatile solvent to produce a solution of soluble organic contaminants from the water sample. This normally includes a dominant fraction of humic and fulvic acids, or even chlorinated versions of these, from treated waters. If ultratrace levels (parts per quadrillion) of the target analytes are to be analyzed, the humic acids must be removed. A common way to achieve this is by oxidation with concentrated sulphuric acid at room temperature[1]. Fractionation can then be undertaken by passing the solution through a series of adsorbing columns. These eluants are then evaporated for final GC/MS detection.

It is recognized that this method is complex and possibly inaccurate. The acid oxidation treatment is capable of destroying compounds of interest while removing the humic fraction. The subsequent fractionation techniques can have low elution recoveries as has been observed in research on the octachlorodibenzo-p-dioxin congener. Thus, large recovery correction factors are common in analytical data.

A further drawback is the complexity of automation which might be attempted in order to avoid manual labour, time and expense. The number of steps and reagents makes automation very difficult to control. The corrosive or solubilizing nature of the reagents requires an expensive apparatus which may be subject to decay.

A highly viable alternative is the extraction by supercritical fluids, developed in the food and chemical processing industries. Essentially, the samples in their chambers may be dried under vacuum and then extracted

automatically under pressure by liquid $CO_2$ at room temperature on a single pressure system[2] (see figure 4).

Aside from reducing opportunities for contamination and greatly simplifying sample handling, the process also eliminates many of the chemical isolation steps. This is because liquid $CO_2$ is capable of extracting small hydrophobic molecules from XAD-2 with 95% recovery at room temperature and operating under a pressure of 2000 psi, without solubilizing the polymeric humic acids. After flashing off liquid $CO_2$, the sample is delivered as a solid deposit of the compounds of interest only. The oxidation step is unnecessary and the only question remaining is the number of fractionation steps required to permit GC/MS detection and identification.

In the present apparatus, the adsorption columns are capable of direct attachment to the pressure line. The filter chambers, however, cannot sustain the pressure. They will be installed in high pressure chambers and held in place by a hydraulic ram. The filter chamber will then be pressurized simultaneously outside and inside, the inside stream operating as the elution system. As a result, both types of chamber can be extracted within 10 to 15 minutes, producing dried samples ready for dissolution in any chosen solvent, followed either by direct GC/MS injection or fractionation prior to injection.



References:

1/ G.L. LeBel, D.T. Williams, J.J. Ryan and B.P.-Y. Lau, "Chlorinated Dioxins and Dibenzofurans in Perspective" (C. Rappe et. al. eds.) (Lewis Publishers, Michigan, 1986) 329-341

2/ M.A. McHugh and V.J. Krukonis, "Supercritical Fluid Extraction", Butterworth Publishers, MA, U.S., 1986.

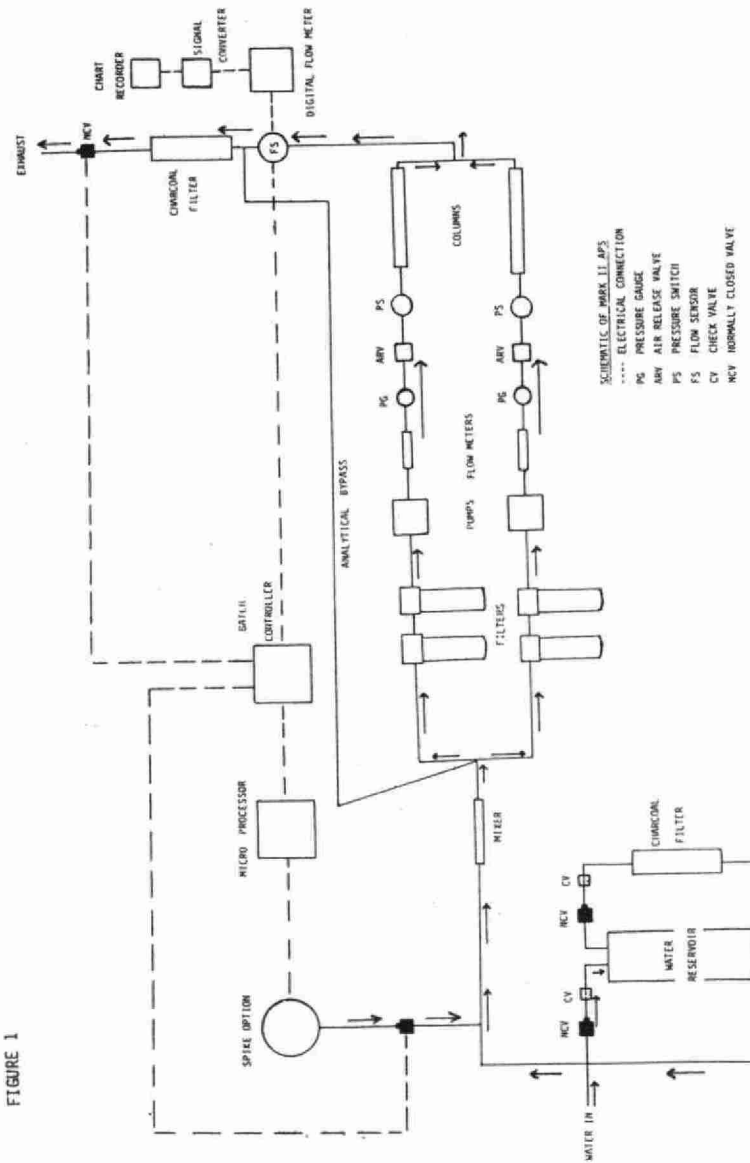



FIGURE 1



FIGURE 2

RIGHT SIDE VIEW

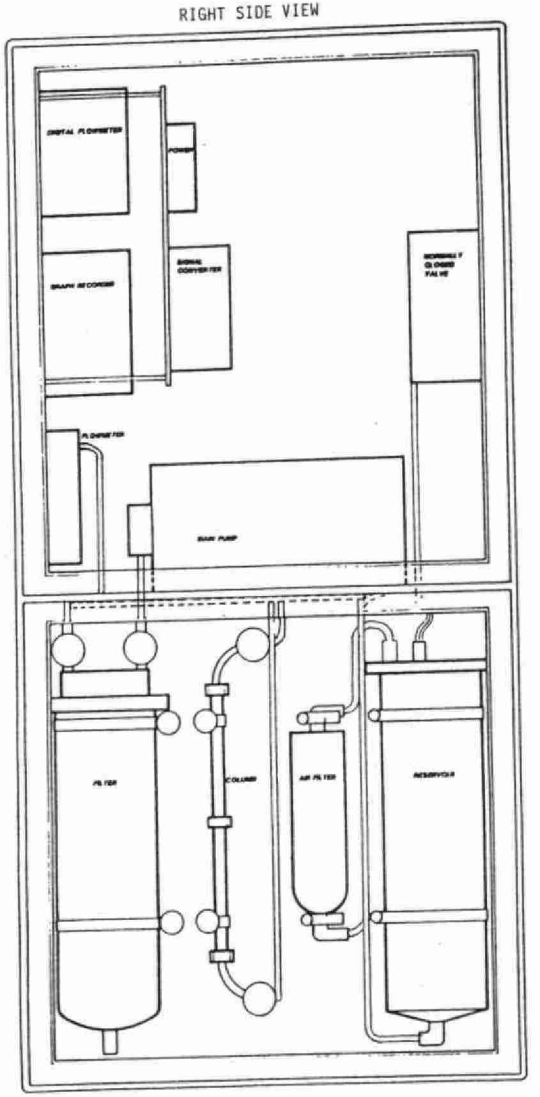
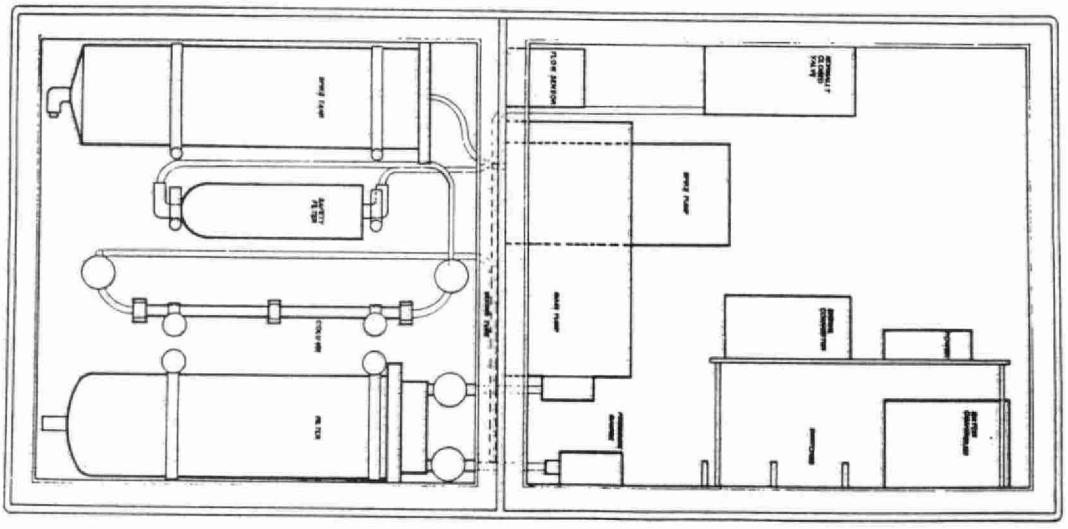


FIGURE 3



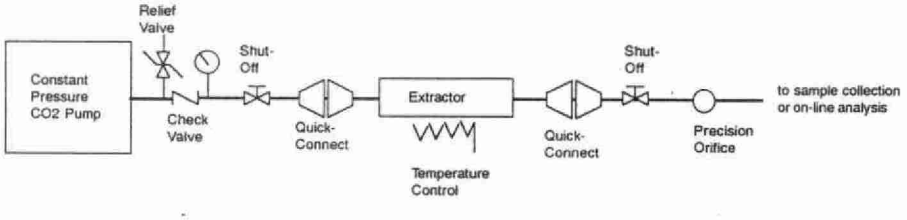
LEFT SIDE VIEW



FIGURE 4

| TITLE: Proposed Cartridge Extraction System | | |
|---|---|---|
| Analytical Technology Marketing Corporation<br>Suite 205, 3701 Chesswood Dr.<br>Downsview, Ont. M3J 2P6 (416) 631-6391 | Drawing Number: WSP-02<br>Drawn By: P. Smith | ATMC<br>SEPARATIONS FOR RESEARCH AND INDUSTRY |

**System Schematic**




**Sample Collection**